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(54) Title: METHOD AND APPARATUS FOR MONITORING AND CONTROLLING CHARACTERISTICS OF PROCESS EFFLUENTS

(57) Abstract

A method for monitoring and controlling a characteristic of process waters or effluent from wood pulp bleaching, pulping and paper making processes utilizing a bleaching agent such as hydrogen peroxide (H_2O_2), $Na_2S_2O_4$, ClO_2 , Cl_2 or O_3 or a pulp delignification process utilizing a delignification agent such as $NaOH$, Na_2S , O_2 , Na_2SO_3 , and various enzymes including ligninase, xylanase, mannanase, laccase, and peroxidase. The method comprises the steps of obtaining at least two measurements of ultraviolet light absorption of the effluent, by taking a first measurement measured at a first wavelength, and a second measurement measured at a second wavelength, then determining a ratio of the two measurements and comparing the ratio to a predetermined interrelationship of the ratio and the characteristic of the effluent, thereby determining the actual value of the characteristic. An apparatus for monitoring a characteristic of an effluent of a process comprising a means for obtaining at least two measurements of ultraviolet light absorption of the effluent, a first measurement measured at the first wavelength, a second measurement measured at a second wavelength. A means is provided to compare the ratio of the two measurements to a predetermined interrelationship of the ratio and the characteristic of the effluent, thereby determining the actual value of the characteristic.

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Method and Apparatus for Monitoring and Controlling Characteristics of Process Effluents

FIELD OF THE INVENTION

5 The present invention relates to the monitoring and controlling of a process using ultraviolet light absorption. In particular, the invention relates to the monitoring and controlling of a wood pulp bleaching, pulping or paper making process by using UV light absorption ratios of the process effluent.

10 BACKGROUND OF THE INVENTION

In many industrial chemical processes, the amount of reactants, or input components, that are used is less than or more than the amount necessary to carry the reaction to the point of obtaining a desired characteristic(s) of the product stream. If too little of the input component is used, often the desired target value of a characteristic from the process is not obtained. Alternatively, if an excessive amount of an input component is used, the desired characteristic may be obtained, but the excess input component is typically released as waste in the effluent of the process. In other cases, excessive amounts of an input component may cause undesirable reactions to occur that produce unwanted characteristics. Further, the wasted input component is economically costly and can become an environmental pollutant if it is released into the environment without being removed or recycled from the effluent.

The difficulty in controlling chemical processes, such as bleaching, in the pulp and paper manufacturing industry can be caused by a number of factors including qualitative and quantitative variability of the pulp or wood furnish, the composition of the process chemicals, and the consistency (% wood or pulp) of the furnish. Further, changing market requirements for paper products may require a paper manufacturing operation to produce a wide variety of paper grades. New paper processing methods, equipment, and chemicals force the paper bleaching operation to adapt to these technical changes while still monitoring various characteristics of the pulp.

It is therefore desirable to be able to precisely control the input components to obtain the desired target characteristic(s) with little waste. To obtain this control, a characteristic of the effluent of an industrial process should be precisely monitored in real time in order to provide feedback control on the amount of input components which should be added to the
5 reactor to avoid under use or excessive use, and waste, of the input component.

For example, in the pulp and paper industry, hydrogen peroxide and the hydroperoxy anion (HO_2G) are important input components for the oxidation and bleaching of wood pulps.
In a typical pulp bleaching plant situation, the control of the bleaching chemicals is based on the brightness of the incoming pulp, the pulp flow, and the target brightness that is to be
10 achieved. The factors of incoming pulp brightness, pulp flow, and target brightness are then used to calculate the amount of bleaching chemicals required to be added to the pulp to achieve a certain final target brightness. In another system, the brightness of the pulp is measured after bleaching chemicals are added and after allowing the reaction to occur for a defined reaction time. The resultant brightness value of the reaction is then measured and
15 is used for feedback regulation of the bleaching chemicals.

Typically with these feedback systems, the amount of hydrogen peroxide that is used exceeds or overshoots the amount necessary to reach a final target characteristic, such as pulp final target brightness, yellowness, residual peroxide, brightness efficiency, yellowness efficiency, and delignification efficiency. The resultant unwanted variation in these pulp
20 characteristics may cause additional processing problems in the pulp and paper processing mill. Further, in the case of peroxide bleaching, excessive use of hydrogen peroxide results in waste hydrogen peroxide in the pulp effluent, which is both costly and environmentally harmful.

In order to solve these problems the prior art has offered various solutions. For
25 example, United States Patent No. 4,878,998 teaches a method for bleaching of mechanical, thermomechanical and chemi-mechanical pulps whereby peroxide bleaching is controlled by the addition of a preset amount of bleaching chemicals at a first bleaching stage, measuring the brightness of the pulp, feed forwardly adjusting the amount of bleaching

chemicals to be added at a second bleaching stage as a function of the measured brightness of the pulp from the first stage, and then bleaching the pulp at the second stage.

Canadian Patent No. 2,081,907 teaches a method and apparatus for determining information characteristics of the concentration of each of at least three intermixed components in kraft liquors having the steps of: identifying detectable characteristics that are detectable in relation to the concentration of the components, developing a mathematical relationship between the component and the characteristics, such as regression analysis, analysing a sample of solution with a UV detector, and then controlling the concentration of each of the three components by using the information from the analysis of the sample.

While current brightness sensors are able to provide a measure of the pulp brightness, they are unable to measure the bleaching efficiency of the bleaching reaction itself. (Bleaching efficiency is the change in brightness of the pulp divided by the residual peroxide in the pulp effluent.) Further, measurement of yellowness efficiency (the change in pulp yellowness divided by the residual peroxide in the pulp effluent) also requires a method by which the residual peroxide in the pulp effluent can be measured.

Unfortunately, it is well known that there is a present lack of an appropriate method or device for the monitoring and control of pulp bleaching reaction characteristics, including pulp final target brightness, yellowness, residual peroxide, brightness efficiency, yellowness efficiency, and delignification efficiency. Also, it is known that pH measurement probes and electrochemical methods of measuring hydrogen peroxide, such as the Kajaani Polarox sensor made by Valmet Automation, can be unreliable under pH conditions which are typically used for pulp brightening reactions.

SUMMARY OF THE INVENTION

In one aspect of the present invention, it provides a method for monitoring a characteristic of an effluent of a process comprising the steps of:

- (a) obtaining at least two measurements of ultraviolet light absorption of the effluent, each at a different wavelength by obtaining:

one measurement of light absorption at a first ultraviolet wavelength;
and
a second measurement of light absorption at a second ultraviolet wavelength; and

5 (b) comparing a ratio of these at least two measurements to a predetermined interrelationship of the ratio and the characteristic of the effluent, to determine the empirical value of the characteristic.

In another aspect of the present invention, it provides a method for monitoring and controlling a characteristic of an effluent comprising the steps of:

10 (a) obtaining at least two measurements of ultraviolet light absorption of the effluent , each at a different wavelength by obtaining:
 one measurement of light absorption at a first ultraviolet wavelength;
 and
 a second measurement of light absorption at a second ultraviolet
15 wavelength;

 (b) comparing a ratio of these two measurements to a predetermined interrelationship of the ratio and the characteristic of the effluent, to determine the empirical value of the characteristic; and

 (c) controlling the characteristic using feedback control whereby one or more feed input components are adjusted in accordance with the determined empirical value of the characteristic, to obtain the desired target measurement
20 of the characteristic.

In another aspect of the present invention provides an apparatus for monitoring a characteristic of an effluent of a process comprising:

25 (a) a means for obtaining at least two measurements of ultraviolet light absorption of the effluent, each at a different wavelength by obtaining:
 one measurement of light absorption at a first ultraviolet wavelength;
 and

a second measurement of light absorption at a second ultraviolet wavelength; and

(b) a means for comparing a ratio of these at least two measurements to a predetermined interrelationship of the ratio and the characteristic of the effluent, to determine the empirical value of the characteristic.

In another aspect, the present inventor provides an apparatus for monitoring and controlling a characteristic of an effluent comprising:

(a) a means for obtaining at least two measurements of ultraviolet light absorption of the effluent, each at a different wavelength by obtaining:

10 one measurement of light absorption at a first ultraviolet wavelength;
and
a second measurement of light absorption at a second ultraviolet wavelength;

(b) a means for comparing a ratio of these two measurements to a predetermined interrelationship of the ratio and the characteristic of the effluent, to determine the empirical value of the characteristic; and

15 (c) a means for controlling the characteristic using feedback control whereby one or more feed input components are adjusted in accordance with the determined empirical value of the characteristic, to obtain the desired target measurement of the characteristic.

20

According to an embodiment of the invention, process waters or effluent is produced from wood pulp bleaching, pulping and paper making processes utilizing a bleaching agent such as hydrogen peroxide (H_2O_2), $Na_2S_2O_4$, ClO_2 , Cl_2 or O_3 , or a pulp delignification process utilizing a delignification agent such as $NaOH$, Na_2S , O_2 , Na_2SO_3 , and various enzymes including ligninase, xylanase, mannanase, laccase, and peroxidase.

BRIEF DESCRIPTION OF DRAWINGS:

The present invention will now be described in more detail, with reference to the appended Figures, wherein:

Figure 1 is a schematic diagram of a preferred embodiment of the present invention.

Figure 2 is a graphical representation of the predetermined interrelationship of the ratio of ultraviolet light absorption at 230 nm and 300 nm ($A_{230\text{ nm}}/A_{300\text{ nm}}$) and the weight percentage value of H_2O_2 (as a weight percentage of dry pulp weight) of the pulp effluent.

5

Figure 3 is a graphical representation of the predetermined interrelationship of the ratio of ultraviolet light absorption at 230 nm and 250 nm ($A_{230\text{ nm}}/A_{250\text{ nm}}$) and the pH value of the pulp effluent for different reaction times.

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Figure 4 is a graphical representation of the predetermined interrelationship of the ratio of ultraviolet light absorption at 280 nm and 350 nm ($A_{280\text{ nm}}/A_{350\text{ nm}}$) and the brightness (ISO) of the pulp after brightening.

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Figure 5 is a graphical representation of actual and predicted values of the brightness (ISO) of spruce wood pulp as a function of pH of spruce wood pulp using a multilinear regression with ratios of ultraviolet light absorption of $A_{230\text{ nm}}/A_{250\text{ nm}}$, $A_{350\text{ nm}}/A_{280\text{ nm}}$ and $A_{230\text{ nm}}/A_{300\text{ nm}}$.

Figure 6 is a graphical representation of actual and predicted values of the residual H_2O_2 (peroxide) concentration in spruce wood pulp effluent as a function of pH of spruce wood pulp using a multilinear regression with ratios of ultraviolet light absorption of $A_{230\text{ nm}}/A_{250\text{ nm}}$, $A_{350\text{ nm}}/A_{280\text{ nm}}$ and $A_{350\text{ nm}}/A_{300\text{ nm}}$.

20

Figure 7 is a graphical representation of actual and predicted values of the delignification efficiency of spruce wood pulp as a function of pH of spruce wood pulp using a multilinear regression and ratios of ultraviolet light absorption of $A_{230\text{ nm}}/A_{250\text{ nm}}$, $A_{350\text{ nm}}/A_{280\text{ nm}}$ and $A_{300\text{ nm}}/A_{280\text{ nm}}$.

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DETAILED DESCRIPTION OF DRAWINGS

Figure 1 is a schematic diagram of a pulp bleaching process utilizing a preferred embodiment of the present invention. As shown in Figure 1, wood pulp 2 is bleached in a bleaching chamber 4, by bleaching agent hydrogen peroxide (H_2O_2), as input component. H_2O_2 flows from reservoir 18 through control valve 16 into the bleaching chamber 4. The

output of the bleaching process is a process effluent 6 which includes both the bleached pulp as well as the bleaching liquor.

A sample of the effluent 6 is diverted to an ultraviolet (UV) light sensor 10 for the purpose of obtaining at least two measurements of UV light absorption of the effluent 6 and
5 then calculating the ratio of the two measurements. The ratio of the UV light absorbance measurements have been found to correlate to various characteristics of the pulp effluent.

For example, characteristics such as pulp brightness, pH, and pulp yellowness, and residual peroxide can be determined through the use of different UV wavelengths in the ratio. It has also been found that different types of wood pulp, such as aspen or spruce, require different
10 UV wavelengths to measure the same characteristic of the effluent. In particular, it may be desirable to select alternative wavelengths which correspond to the peaks and valleys of the UV absorbance spectra for a particular characteristic of the specific effluent.

The bleaching process causes structural changes in the lignin or extractive components of the pulp including ionization of the phenolic groups of the lignin molecule.
15

Lignin degradation typically results in an increase in the number of phenolic groups that can be ionized by changes in pH. As a result, the relative amount of ionized phenolic groups usually depends on the extent of lignin degradation and pH. It has been found that UV light absorbance of the pulp effluent at wavelengths of 230 "5 nm ($A_{230+5\text{nm}}$), 250 "5 nm ($A_{250+5\text{nm}}$),
300 "10 nm ($A_{300+10\text{nm}}$), and 350 nm ($A_{350\text{nm}}$) varies in relation to the degree of ionization
20 of phenolic groups in the lignin molecule. Therefore, UV light absorption at these wavelengths provides a means to measure a combination of the degree of lignin degradation and pH. In order to measure pH or lignin degradation itself, one must understand the conditions of the particular bleaching process and the pH range over which the variable (pH or lignin degradation) is to be measured. These wavelengths are most effective to measure
25 pH at pH values which are close to the pK_a values of the lignin components. For example, it is more effective to measure pH in ranges which are close to the pK_a of the phenolic structural groups ($pK_a=10.0$), or the p-hydroxybenzoic acid groups ($pK_a=9.0$), the phenolic groups (with a carbonyl group) ($pK_a=7.4$), or a carboxylic acid group ($pK_a=4.8$). Alternatively, these wavelengths are most effective to measure lignin degradation

where the pH is 10.5 or greater. For example, in the kraft pulping processes which generally occur at pH 10.5 and greater, UV measurements taken at these wavelengths generally correlate with the extent of lignin degradation.

Further, it has been also found that UV light absorption at wavelengths between 270
5 nm and 280 nm ($A_{270-280\text{nm}}$) is invariant with the structure of the lignin molecule and provides a measure of the delignification of the pulp (i.e. delignification is a term referring to the removal of lignin and lignin components from the pulp.). Additionally, UV light absorbance at 300 nm generally varies with changes in pH.

Further, the yellowness of the pulp, caused by the existence of coloured compounds,
10 generally corresponds to UV light absorbance at wavelengths of 330 nm, 350 nm, 400 nm, and 450 nm ($A_{330\text{nm}}$, $A_{350\text{nm}}$, $A_{400\text{nm}}$, and $A_{450\text{nm}}$). Molecular structures whose presence has a high correlation to UV light absorbance at these wavelengths include quinones, α -carbonyl phenolic structures, coniferaldehyde structures, stilbenes and lignin metal (iron or manganese) complexes.

15 According to the present invention, two UV light absorbance measurements are obtained from the pulp effluent and a ratio is calculated from these measurements. In the case of pulp brightness, a ratio is calculated using a first measurement of UV light absorption at a wavelength of either 230 " 5 nm, 250 " 5 nm, 300 " 10 nm, and 350 nm. A second measurement is obtained at a different wavelength of 230 nm or 270 nm to 280 nm.
20 The ratio of the first and second measurements provides an indirect measurement of pulp brightness by measurement of properties of the pulp effluent: the concentration of hydrogen peroxide, the ionization of the lignin phenolic groups, and the colour of the pulp effluent relative to amount of lignin remaining in the pulp (as a result of delignification).

In the case of pulp yellowness, a ratio is calculated using a first measurement of UV
25 light absorption of the pulp effluent at a wavelength of 330 nm, 350 nm, 400 nm, and 450 nm. A second measurement is obtained at 270 nm to 280 nm. The ratio of these two measurements provides a measurement of pulp yellowness by measurement of the coloured compounds relative to the amount of lignin remaining in the pulp (as a result of delignification).

Further, for measuring residual peroxide in the pulp effluent, one of these measurements is made at a first wavelength, such as 230 nanometres (nm), while the second measurement is made at a different wavelength, such as 280 nm or 300 nm. The ratio of these measurements provides a measure of the amount of peroxyxyl anion in the pulp effluent,
5 thereby indirectly measuring the residual peroxide in the pulp effluent.

In the case of measuring the pH of the pulp effluent, one of these measurements is made at a first wavelength, 230 nm or 300 nm, while the second measurement is made at 250 nm or 280 nm. It is believed that as the lignin phenolic groups are ionized, the UV absorbance for given chromophore shifts up to longer wavelengths by approximately 20-30
10 nm. For example, the UV light absorption of a chromophore at 230 nm at pH 9 will shift up to absorb UV light at approximately 250 nm at pH 11. Similarly, the absorbance spectra of a chromophore at 300 nm at pH 11 will shift down to absorb light at 270 nm at a lower pH, as a result of protonation of the chromophore. It is believed that this relative shifting of
15 UV absorbance as a result of ionization or protonation allows the ratio of UV absorbance at these wavelengths to correlate to the pH of the pulp effluent.

According to a preferred embodiment, the effluent 6 is filtered first by a coarse filter (1 mm mesh) and then filtered by a 0.2 micron filter (Mott 700-1/2-24-0.5) filter to remove colloidal material from the pulp effluent. If the colloidal material is not removed from the effluent, the resultant turbidity may offset the UV absorbance and affect the UV ratios of the
20 present invention.

The pulp bleaching liquor is then diverted into a sample cell, such as a Helma 170-QS 0.2 mm sample cuvette. The cuvette is illuminated by a xenon strobe light, such as an Ocean Optics PX-1. The resultant light output that is not absorbed is channelled through a fibre optic cable, such as a 400 micron UV/VIS fibre optic cable, to a UV spectrophotometer,
25 such as an Ocean Optics PC1000 which has been optimized for measuring light between 200 and 450 nm , the output of which is fed to computer 12.

Computer 12 calculates a mathematical relationship between two or more UV measurements, which is a ratio or combination of ratios in this preferred embodiment.

Moreover, computer 12 stores in its memory a predetermined interrelationship between the ratio and a characteristic of the effluent.

For example, Figure 2 shows the predetermined interrelationship of the ratio of ultraviolet light absorption at 230 nm and 300 nm ($A_{230\text{ nm}}/A_{300\text{ nm}}$) and residual peroxide in the effluent. The residual peroxide may be expressed as a residual weight percentage value of the dry pulp weight of the pulp effluent. Figure 2 shows this predetermined interrelationship for two types of wood pulp, spruce and aspen, both of which illustrate a substantially linear interrelationship. As will be appreciated by those skilled in the art, Figure 2 may be created in the laboratory by repeated measurements of UV light absorption ratios and the weight percentage value of H_2O_2 .

Computer 12 acts as a comparing means for comparing the ratio with the predetermined interrelationship of Figure 2. This comparison step determines the actual empirical value of the residual weight percentage of H_2O_2 , the characteristic of the effluent being monitored.

According to this preferred embodiment, computer 12 determines whether to send a feedback signal 14 to control valve 16 to adjust the amount of H_2O_2 being fed into the bleaching process taking place in bleaching chamber 4. Thus, computer 12 together with control valve 16 act as a means for adjusting the amount of input component, such as H_2O_2 , according to the value of the characteristic of the effluent 6, H_2O_2 concentration, which was determined by the ratio of the two UV absorption measurements.

Thus, as shown by the preferred embodiment of the invention, shown in Figures 1 and 2, the disclosed invention permits a real time feedback control of a pulp bleaching process. The feedback system provides sufficient H_2O_2 to the pulp bleaching process without producing excessive waste residual H_2O_2 or pollution.

It is contemplated that other input components, such as NaOH , MgSO_4 , or a chelating agent, such as DTPA (diethylenetriamine pentaacetic acid), may be added to the bleaching reaction in reduced or increased amounts in accordance with this feedback system.

Figure 3 shows a graphical representations of the predetermined interrelationships of the ratio of UV light absorption at 230 nm and 250 nm ($A_{230\text{ nm}}/A_{250\text{ nm}}$) and the pH value

of the pulp effluent for different reaction times. As shown, the wavelengths chosen for measuring UV absorption are 230 nm and 250 nm. Thus, the monitoring of the pH of pulp effluent can be accomplished by comparing the predetermined interrelationship shown in Figure 3 with a real time UV absorption ratio measured from the pulp effluent.

5 Figure 4 shows a graphical representation of the interrelationship of a UV absorbance ratio and pulp brightness. In this case the ratio of UV absorption measurements is $A_{280\text{ nm}}/A_{350\text{ nm}}$. It is contemplated that the increase in the ratio corresponds to a reduction in the amount of UV-light absorbing carbonyl containing components in the bleached pulp effluent. Brightness was standardized using pulp brightness measuring procedures which are well
10 known in the art and are described in detail in procedure method TAPPI T 452 om-92 entitled *Brightness of Pulp, Paper, and Paperboard*. According to this standard method, it is understood that pulp brightness may be expressed as a percentage of the reflectance of magnesium oxide based upon standard optical property procedures. Further, as stated above, other useful UV absorption wavelength ratios for measuring pulp brightness have
15 been found to including 280nm/300nm and 230nm/250nm.

As stated earlier, UV absorption wavelength ratios including 280nm/350nm have been found useful for monitoring the yellowness of the pulp. Standard pulp yellowness measuring procedures are well known in the art and are described in further detail in procedure method TAPPI T524 om-86 entitled *L, a, b, 45E 0E Colorimetry of White and
20 Near-White Paper and Paperboard*.

Figures 5, 6, and 7 were obtained show the predictive value of using the UV absorbance ratios of the present invention with for measuring brightness, residual peroxide, and delignification efficiency. To obtain these graphs, pulp was bleached under different pH conditions. A sample of pulp effluent was removed from the pulp at 3 minutes (3 min.),
25 filtered, and then the UV absorbance of the filtered effluent was measured. A series of five different UV ratios were obtained as a function of pH at three minutes into the bleaching reaction ($A_{230\text{ nm}}/A_{250\text{ nm}}$, $A_{230\text{ nm}}/A_{300\text{ nm}}$, $A_{350\text{ nm}}/A_{280\text{ nm}}$, $A_{300\text{ nm}}/A_{280\text{ nm}}$, $A_{350\text{ nm}}/A_{300\text{ nm}}$). The final pulp brightness, residual peroxide, and delignification efficiency of the reaction was then measured after 90 minutes into the bleaching reaction. Multiple regression analysis.

using a forward stepwise multiple regression, was conducted using these UV ratios to determine the best combination of these ratios and coefficients, (i.e. a predetermined relationship) which best predicted the final property of the pulp (i.e. optical properties and other descriptors of bleaching including delignification efficiency and residual peroxide).

5 As shown in the graphs, the present invention can use this predetermined relationship to determine a pulp property (final brightness, delignification efficiency, or residual peroxide) using a minimum number of UV light absorbance ratio measurements obtained early (at 3 min.) in the bleaching process.

Figure 5 shows a graphical representation of actual and predicted values of the
10 brightness of spruce wood pulp as a function of pH of spruce wood pulp. A predetermined empirical relationship of brightness as a function of pH was created using effluent extracted at 3 minutes after initiation of the brightening/bleaching reaction using H₂O₂. As discussed, this data was analyzed by standard forward stepwise multiple regression to predict brightness at 90 minutes after the bleaching reaction started. The results of the forward stepwise
15 multiple regression analysis indicates that the predicted brightness at 90 minutes after initiation of the bleaching/brightening reaction fits the general equation:

$$\text{Brightness (@ 90 min.)} = a + b * A_{230 \text{ nm}} / A_{250 \text{ nm}} + c * A_{350 \text{ nm}} / A_{280 \text{ nm}} + d * A_{230 \text{ nm}} / A_{300 \text{ nm}}$$

Multilinear regression provided the following coefficients:

$$\text{Brightness (@ 90 min.)} = 95.75 + 44.99 A_{230 \text{ nm}} / A_{250 \text{ nm}} - 322.6 A_{350 \text{ nm}} / A_{280 \text{ nm}} - 4.980 A_{230 \text{ nm}} / A_{300 \text{ nm}}$$

20 As shown in this equation, the best relationship is given by combining the above three UV ratios. This equation was found to be useful in predicted the final property, brightness, using UV absorbances obtained from the pulp effluent at 3 minutes after initiation of the bleaching reaction. Figure 5 shows a high level of reliability between the predicted and actual values
25 of brightness at different pH values.

Figure 6 shows a graphical representation of actual and predicted values of the residual H₂O₂ (expressed as a percentage weight) in spruce wood pulp as a function of the pH of spruce wood pulp. A predetermined empirical relationship of residual H₂O₂ as a function of pH was created using effluent extracted at 3 minutes after initiation of the

brightening/bleaching reaction using H₂O₂. As discussed, this data was analyzed by standard forward stepwise multiple regression to predict residual H₂O₂ at 90 minutes after the bleaching reaction started. The results of the forward stepwise multiple regression analysis indicates that the predicted residual H₂O₂ at 90 minutes after initiation of the
5 bleaching/brightening reaction fits the general equation:

$$\text{Residual H}_2\text{O}_2(@ 90 \text{ min.}) = a + b * A_{230 \text{ nm}} / A_{250 \text{ nm}} + c * A_{350 \text{ nm}} / A_{280 \text{ nm}} + d * A_{350 \text{ nm}} / A_{300 \text{ nm}}$$

Multilinear regression provided the following coefficients:

$$\text{Residual H}_2\text{O}_2(@ 90 \text{ min.}) = 511 + 104.24A_{230 \text{ nm}} / A_{250 \text{ nm}} - 5130.7A_{350 \text{ nm}} / A_{280 \text{ nm}} + 1521.3A_{350 \text{ nm}} / A_{300 \text{ nm}}$$

10 As shown in this equation, the best relationship is given by combining the above three UV ratios. Figure 6 shows a high level of reliability between the predicted and actual values of residual H₂O₂ at different pH values.

Figure 7 shows a graphical representation of actual and predicted values of the delignification efficiency of spruce wood pulp as a function of the pH of spruce wood pulp.

15 A predetermined empirical relationship of delignification efficiency as a function of pH was created using effluent extracted at 3 minutes after initiation of the brightening/bleaching reaction using H₂O₂. As discussed, this data was analyzed by standard forward stepwise multiple regression to predict delignification efficiency at 90 minutes after the bleaching reaction started. The results of the forward stepwise multiple regression analysis indicates
20 that the predicted delignification efficiency at 90 minutes after initiation of the bleaching/brightening reaction fits the general equation:

$$\text{delignification efficiency}(@ 90 \text{ min.}) = a + b * A_{230 \text{ nm}} / A_{250 \text{ nm}} + c * A_{350 \text{ nm}} / A_{280 \text{ nm}} + d * A_{300 \text{ nm}} / A_{280 \text{ nm}}$$

Multilinear regression provided the following coefficients:

$$25 \text{ delignification efficiency} (@ 90 \text{ min.}) = 151.01 + 62.253A_{230 \text{ nm}} / A_{250 \text{ nm}} - 772.08A_{350 \text{ nm}} / A_{280 \text{ nm}} - 94.107A_{300 \text{ nm}} / A_{280 \text{ nm}}$$

As shown, the best relationship is given by combining the above three UV ratios. Figure 7 shows a high level of reliability between the predicted and actual values of delignification efficiency at different pH values.

Similar experiments using the same bleaching reaction conditions have also been obtained for aspen pulp. The results of the forward stepwise multiple regression analysis indicates that the predicted brightness, residual H₂O₂, and delignification efficiency at 90 minutes after initiation of the bleaching/brightening reaction fits the following equations:

5 Brightness(@ 90 min.) = 78.33 - 86.56A_{350 nm}/A_{280 nm} + 9.157A_{230 nm}/A_{280 nm}

Residual H₂O₂(@ 90 min.) = -376.24 + 239.30A_{230 nm}/A_{250nm}

Delignification efficiency (@ 90 min.) = 31.10 - 17.73A_{350 nm}/A_{300 nm}

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It will be appreciated that while the embodiments of Figures 1 to 7 teach the use of some UV absorption wavelength ratios to determine specific properties an industrial wood pulp bleaching process, it is contemplated that other combinations of the disclosed absorbance ratios may also be used to monitor and control various other characteristics in the 15 pulp bleaching process. Also, the disclosed absorbance ratios may undergo further statistical analysis including multiple regression analysis to determine other useful mathematical relationships which permit the monitoring and control of various characteristics of the pulp bleaching process.

The above-described embodiments of the invention are intended to be examples of 20 the present invention and alterations and modifications may be affected thereto, by those of skill in the art, without departing from the scope of the invention which is defined solely by the claims appended hereto.

I claim:

1. A method for monitoring a characteristic of an effluent of a process comprising the steps of:

5 (a) obtaining at least two measurements of ultraviolet light absorption of the effluent, each at a different wavelength by obtaining:
one measurement of light absorption at a first ultraviolet wavelength; and
a second measurement of light absorption at a second different ultraviolet wavelength; and

10 (b) comparing a ratio of these at least two measurements to a predetermined interrelationship of the ratio and the characteristic of the effluent, to determine the empirical value of the characteristic.

2. A method for monitoring and controlling a characteristic of an effluent as claimed
15 in claim 1 and further comprising the step of controlling the characteristic using feedback control whereby one or more feed input components are adjusted in accordance with the determined empirical value of the characteristic, to obtain a desired target measurement of the characteristic.

20 3. A method for monitoring a characteristic of an effluent of a process comprising the steps of:

25 (a) obtaining at least two measurements of ultraviolet light absorption of the effluent, each at a different wavelength by obtaining:
one measurement of light absorption at a first ultraviolet wavelength; and
a second measurement of light absorption at a second different ultraviolet wavelength; and

 (b) comparing a mathematical combination of more than one ratio of these at least two measurements to a predetermined interrelationship of said more

than one ratio and the characteristic of the effluent, to determine the empirical value of the characteristic.

4. A method for monitoring and controlling a characteristic of an effluent as claimed
5 in claim 3 and further comprising the step of controlling the characteristic using feedback control whereby one or more feed input components are adjusted in accordance with the determined empirical value of the characteristic, to obtain a desired target measurement of the characteristic.
- 10 5. A method according to claim 2 wherein said effluent is produced by a wood pulp bleaching process.
6. A method according to claim 4 wherein said effluent is produced by a wood pulp bleaching process.
15
7. A method according to claim 2 wherein said effluent is produced by a wood pulp delignification process.
8. A method according to claim 4 wherein said effluent is produced by a wood pulp
20 delignification process.
9. A method according to claim 5 wherein said predetermined relationship is determined by multiple regression analysis.
- 25 10. A method according to claim 6 wherein said predetermined relationship is determined by multiple regression analysis.

11. A method according to claim 7 wherein said predetermined relationship is determined by multiple regression analysis.
12. A method according to claim 8 wherein said predetermined relationship is determined
5 by multiple regression analysis.
13. A method according to claim 5 wherein said predetermined interrelationship is a substantially linear relationship between said ratio and said characteristic of said effluent.
- 10 14. A method according to claim 6 wherein said predetermined interrelationship is a substantially linear relationship between said ratio and said characteristic of said effluent.
15. A method according to claim 5 wherein said wood pulp bleaching process utilizes a peroxide bleaching agent.
- 15 16. A method according to claim 6 wherein said wood pulp bleaching process utilizes a peroxide bleaching agent.
17. A method according to claim 5 wherein said wood pulp bleaching process utilizes a
20 bleaching agent selected from the group consisting of hydrogen peroxide (H_2O_2), ClO_2 , Cl_2 and O_3 , $Na_2S_2O_4$.
18. A method according to claim 6 wherein said wood pulp bleaching process utilizes a
bleaching agent selected from the group consisting of hydrogen peroxide (H_2O_2), ClO_2 , Cl_2
25 and O_3 , $Na_2S_2O_4$.
19. A method according to claim 7 wherein said wood pulp delignification process utilizes a delignification agent selected from the group consisting of $NaOH$, Na_2S , O_2 ,

Na₂SO₃, and various enzymes including ligninase, xylanase, mannanase, laccase, and manganese peroxidase.

20. A method according to claim 8 wherein said wood pulp delignification process
5 utilizes a delignification agent selected from the group consisting of NaOH, Na₂S, O₂, Na₂SO₃, and various enzymes including ligninase, xylanase, mannanase, laccase, and manganese peroxidase.
21. A method according to claim 15 wherein said first wavelength being selected from
10 the range 230 nm to 260 nm and said second wavelength being selected from the range 280 nm to 500 nm.
22. A method according to claim 16 wherein said first wavelength being selected from
the range 230 nm to 260 nm and said second wavelength being selected from the range 280
15 nm to 500 nm.
23. A method according to claim 15 wherein said first wavelength is 230 and said
second wavelength is selected from the group consisting of 280 or 300 nm and said
characteristic is the amount of peroxy anion in the effluent.
20
24. A method according to claim 16 wherein said first wavelength is 230 nm and said
second wavelength is selected from the group consisting of 280 or 300 nm and said
characteristic is the amount of peroxy anion in the effluent.
25. 25. A method according to claim 15 wherein said first wavelength is selected from the
group consisting of 230 nm or 300 nm and said second wavelength is selected from the group
consisting of 250 nm or 280 nm and said characteristic is pH

26. A method according to claim 16 wherein said first wavelength is selected from the group consisting of 230 nm or 300 nm and said second wavelength is selected from the group consisting of 250 nm or 280 nm and said characteristic is pH

5 27. A method according to claim 15 wherein said first wavelength is selected from the group consisting of 230"5 nm, 250 "5 nm, 300 "10 nm, and 350 nm and said second wavelength is 230 or the range 270nm to 280 nm and said characteristic is degree of ionization of phenolic groups in the pulp effluent relative to the amount of lignin in the effluent.

10

28. A method according to claim 15 wherein said first wavelength is selected from the group consisting of 230 nm or 350 nm and said second wavelength is selected from the group consisting of 250 nm, 280 nm or 300 nm and said characteristic is pulp brightness.

15

29. A method according to claim 16 wherein said first wavelength is selected from the group consisting of 230"5 nm, 250 "5 nm, 300 "10 nm, and 350 nm and said second wavelength is 230 or the range 270nm to 280 nm and said characteristic is degree of ionization of phenolic groups in the pulp effluent relative to the amount of lignin in the effluent.

20

30. A method according to claim 16 wherein said first wavelength is selected from the group consisting of 230 nm or 350 nm and said second wavelength is selected from the group consisting of 250 nm, 280 nm or 300 nm and said characteristic is pulp brightness.

25

31. A method according to claim 15 wherein said first wavelength is selected from the group consisting of 230 nm, 300 nm, and 350 nm and said second wavelength is 250 nm, 280 nm or 300 nm said characteristic is residual hydrogen peroxide in the pulp effluent.

32. A method according to claim 15 wherein said first wavelength is selected from the group consisting of 230 nm, 300 nm, and 350 nm and said second wavelength is 250 nm, 280 nm or 300 nm said characteristic is delignification efficiency.

5 33. A method according to claim 15 wherein said first wavelength is selected from the group consisting of 330 nm, 350 nm, 400 nm, and 450 nm and said second wavelength is selected from the range 270nm to 280 nm and said characteristic is pulp yellowness relative to amount of lignin in the pulp.

10 34. A method according to claim 16 wherein said first wavelength is selected from the group consisting of 330 nm, 350 nm, 400 nm, and 450 nm and said second wavelength is selected from the range 270nm to 280 nm and said characteristic is pulp yellowness relative to amount of lignin in the pulp.

15 35. A method according to claim 16 wherein said input component is selected from the group consisting of H₂O₂, NaOH, MgSO₄, or DTPA (diethylenetriamine pentaacetic acid).

36. An apparatus for monitoring a characteristic of an effluent of a process comprising:

(a) a means for obtaining at least two measurements of ultraviolet light absorption of the effluent, each at a different wavelength by obtaining:
20 one measurement of light absorption at a first ultraviolet wavelength; and a second measurement of light absorption at a second different ultraviolet wavelength; and
(b) a means for comparing a ratio of these at least two measurements to a predetermined interrelationship of the ratio and the characteristic of the effluent, to determine the empirical value of the characteristic.
25

37. An apparatus for monitoring and controlling a characteristic of an effluent as claimed in claim 36 and further comprising a means for controlling the characteristic using feedback

control whereby one or more feed input components are adjusted in accordance with the determined empirical value of the characteristic, to obtain a desired target measurement of the characteristic.

5 38. An apparatus for monitoring a characteristic of an effluent of a process comprising:

- (a) a means for obtaining at least two measurements of ultraviolet light absorption of the effluent, each at a different wavelength by obtaining:
one measurement of light absorption at a first ultraviolet wavelength; and
10 a second measurement of light absorption at a second different ultraviolet wavelength; and
- (b) a means for comparing a mathematical combination of more than one ratio of these at least two measurements to a predetermined interrelationship of said more than one ratio and the characteristic of the effluent, to determine
15 the empirical value of the characteristic.

20 39. An apparatus for monitoring and controlling a characteristic of an effluent as claimed in claim 38 and further comprising a means for controlling the characteristic using feedback control whereby one or more feed input components are adjusted in accordance with the determined empirical value of the characteristic, to obtain a desired target measurement of the characteristic.

25 40. An apparatus according to claim 37 wherein said effluent is produced by a wood pulp bleaching process.

41. An apparatus according to claim 39 wherein said effluent is produced by a wood pulp bleaching process.

42. An apparatus according to claim 37 wherein said effluent is produced by a wood pulp delignification process.

43. An apparatus according to claim 39 wherein said effluent is produced by a wood pulp
5 delignification process.

44. An apparatus according to claim 40 wherein said predetermined relationship is determined by multiple regression analysis.

10 45. An apparatus according to claim 41 wherein said predetermined relationship is determined by multiple regression analysis.

46. An apparatus according to claim 42 wherein said predetermined relationship is determined by multiple regression analysis.

15 47. An apparatus according to claim 43 wherein said predetermined relationship is determined by multiple regression analysis.

48. An apparatus according to claim 40 wherein said predetermined interrelationship is
20 a substantially linear relationship between said ratio and said characteristic of said effluent.

49. An apparatus according to claim 41 wherein said predetermined interrelationship is a substantially linear relationship between said ratio and said characteristic of said effluent.

25 50. An apparatus according to claim 44 wherein said wood pulp bleaching process utilizes a peroxide bleaching agent.

51. An apparatus according to claim 45 wherein said wood pulp bleaching process utilizes a peroxide bleaching agent.

52. An apparatus according to claim 44 wherein said wood pulp bleaching process utilizes a bleaching agent selected from the group consisting of hydrogen peroxide (H_2O_2), ClO_2 , Cl_2 and O_3 , $Na_2S_2O_4$.

5

53. An apparatus according to claim 45 wherein said wood pulp bleaching process utilizes a bleaching agent selected from the group consisting of hydrogen peroxide (H_2O_2), ClO_2 , Cl_2 and O_3 , $Na_2S_2O_4$.

10 54. An apparatus according to claim 42 wherein said wood pulp delignification process utilizes a delignification agent selected from the group consisting of $NaOH$, Na_2S , O_2 , Na_2SO_3 , and various enzymes including ligninase, xylanase, mannanase, laccase, and manganese peroxidase.

15 55. An apparatus according to claim 43 wherein said wood pulp delignification process utilizes a delignification agent selected from the group consisting of $NaOH$, Na_2S , O_2 , Na_2SO_3 , and various enzymes including ligninase, xylanase, mannanase, laccase, and manganese peroxidase.

20 56. An apparatus according to claim 44 wherein said first wavelength being selected from the range 230 nm to 260 nm and said second wavelength being selected from the range 280 nm to 500 nm.

25 57. An apparatus according to claim 45 wherein said first wavelength being selected from the range 230 nm to 260 nm and said second wavelength being selected from the range 280 nm to 500 nm.

58. An apparatus according to claim 44 wherein said first wavelength is 230 and said second wavelength is selected from the group consisting of 280 or 300 nm and said characteristic is the amount of peroxy anion in the effluent.

5 59. An apparatus according to claim 45 wherein said first wavelength is 230 nm and said second wavelength is selected from the group consisting of 280 or 300 nm and said characteristic is the amount of peroxy anion in the effluent.

10 60. An apparatus according to claim 44 wherein said first wavelength is selected from the group consisting of 230 nm or 300 nm and said second wavelength is selected from the group consisting of 250 nm or 280 nm and said characteristic is pH

15 61. An apparatus according to claim 45 wherein said first wavelength is selected from the group consisting of 230 nm or 300 nm and said second wavelength is selected from the group consisting of 250 nm or 280 nm and said characteristic is pH

20 62. An apparatus according to claim 44 wherein said first wavelength is selected from the group consisting of 230"5 nm, 250 "5 nm, 300 "10 nm, and 350 nm and said second wavelength is 230 or the range 270nm to 280 nm and said characteristic is degree of ionization of phenolic groups in the pulp effluent relative to the amount of lignin in the effluent.

25 63. An apparatus according to claim 44 wherein said first wavelength is selected from the group consisting of 230 nm or 350 nm and said second wavelength is selected from the group consisting of 250 nm, 280 nm or 300 nm and said characteristic is pulp brightness.

64. An apparatus according to claim 45 wherein said first wavelength is selected from the group consisting of 230"5 nm, 250 "5 nm, 300 "10 nm, and 350 nm and said second wavelength is 230 or the range 270nm to 280 nm and said characteristic is degree of

ionization of phenolic groups in the pulp effluent relative to the amount of lignin in the effluent.

65. An apparatus according to claim 45 wherein said first wavelength is selected from
5 the group consisting of 230 nm or 350 nm and said second wavelength is selected from the group consisting of 250 nm, 280 nm or 300 nm and said characteristic is pulp brightness.

66. An apparatus according to claim 44 wherein said first wavelength is selected from the group consisting of 230 nm, 300 nm, and 350 nm and said second wavelength is 250
10 nm, 280 nm or 300 nm said characteristic is residual hydrogen peroxide in the pulp effluent.

67. An apparatus according to claim 44 wherein said first wavelength is selected from the group consisting of 230 nm, 300 nm, and 350 nm and said second wavelength is 250 nm,
280 nm or 300 nm said characteristic is delignification efficiency.

15

68. An apparatus according to claim 44 wherein said first wavelength is selected from the group consisting of 330 nm, 350 nm, 400 nm, and 450 nm and said second wavelength is selected from the range 270nm to 280 nm and said characteristic is pulp yellowness relative to amount of lignin in the pulp.

20

69. An apparatus according to claim 45 wherein said first wavelength is selected from the group consisting of 330 nm, 350 nm, 400 nm, and 450 nm and said second wavelength is selected from the range 270nm to 280 nm and said characteristic is pulp yellowness relative to amount of lignin in the pulp.

25

70. An apparatus according to claim 45 wherein said input component is selected from the group consisting of H₂O₂, NaOH, MgSO₄, or DTPA (diethylenetriamine pentaacetic acid).

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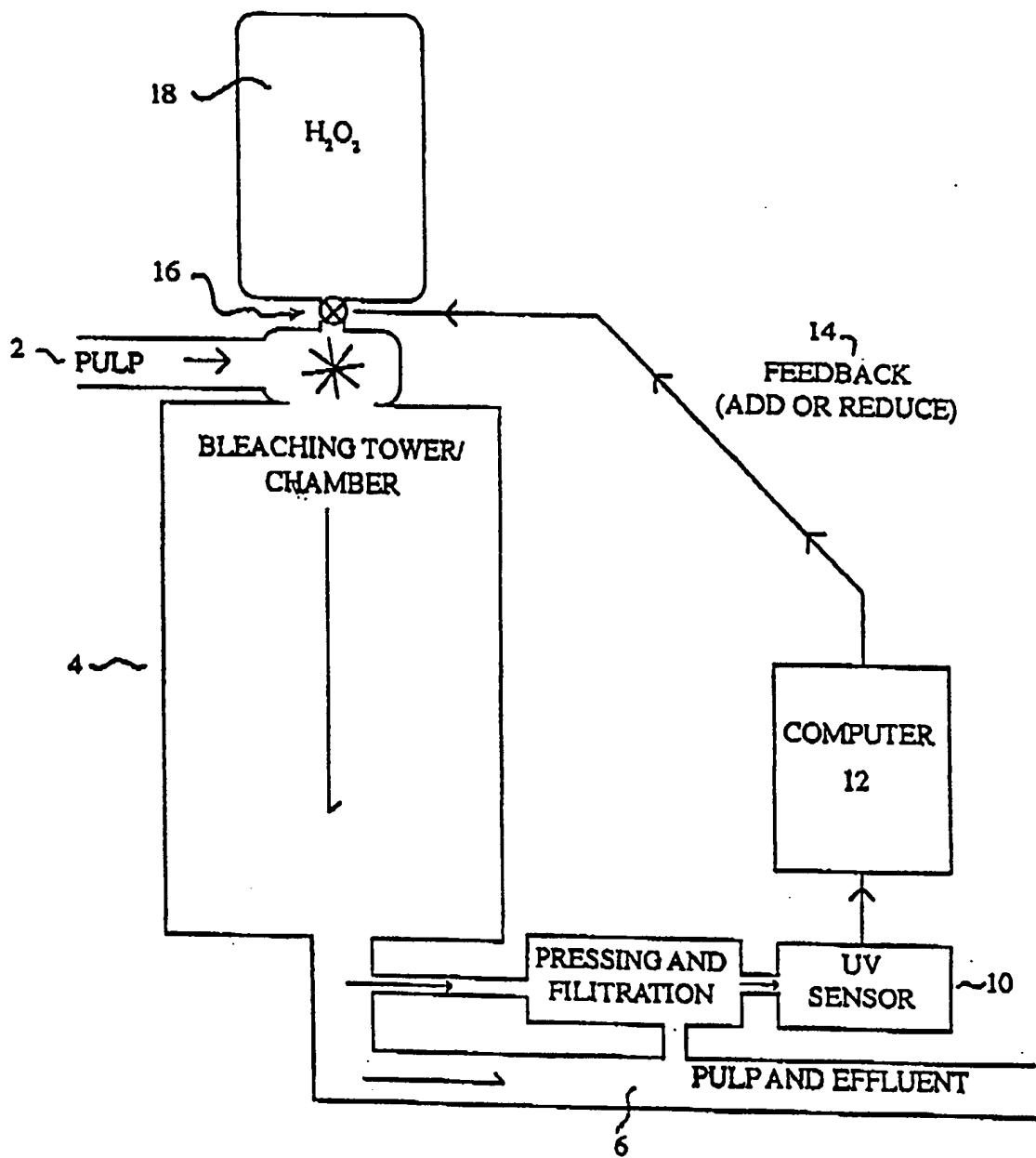


Figure 1.

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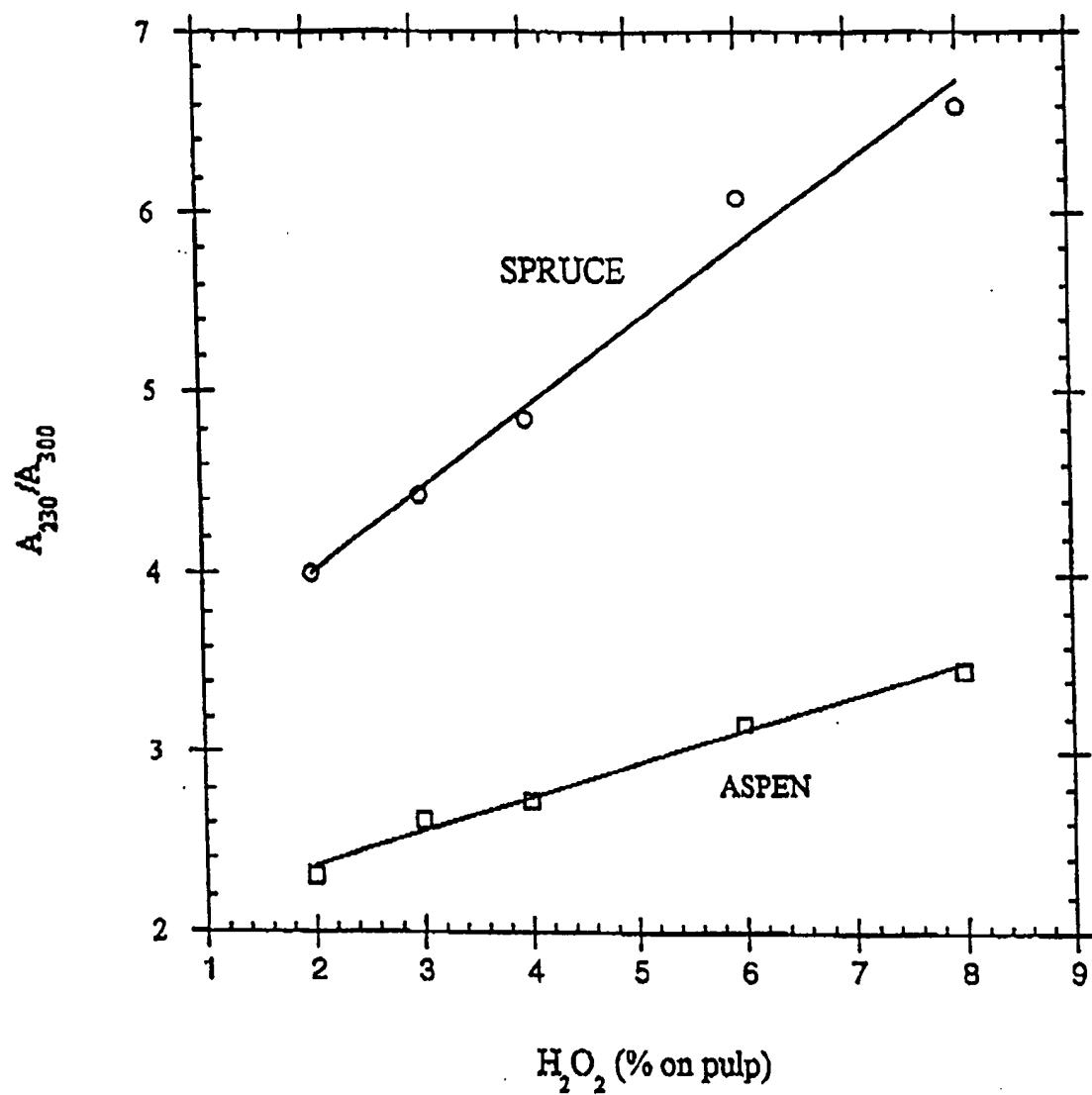


Figure 2. Absorbance ratio A_{230}/A_{300} as a function of initial charge of H_2O_2 .

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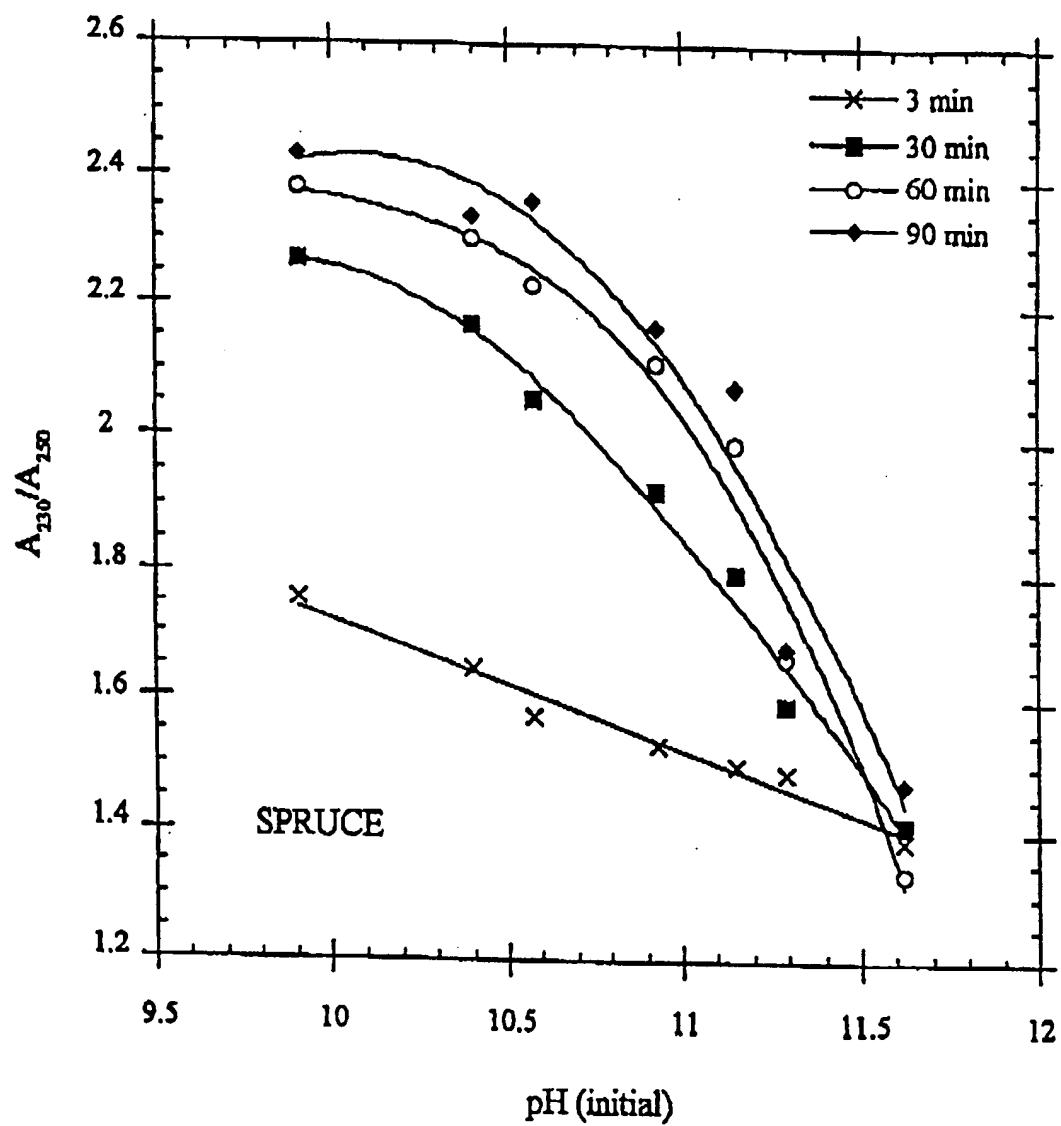


Figure 3. Absorbance ratio A_{230}/A_{250} for spruce pulp as a function of the H_2O_2 bleaching reaction pH at different times.

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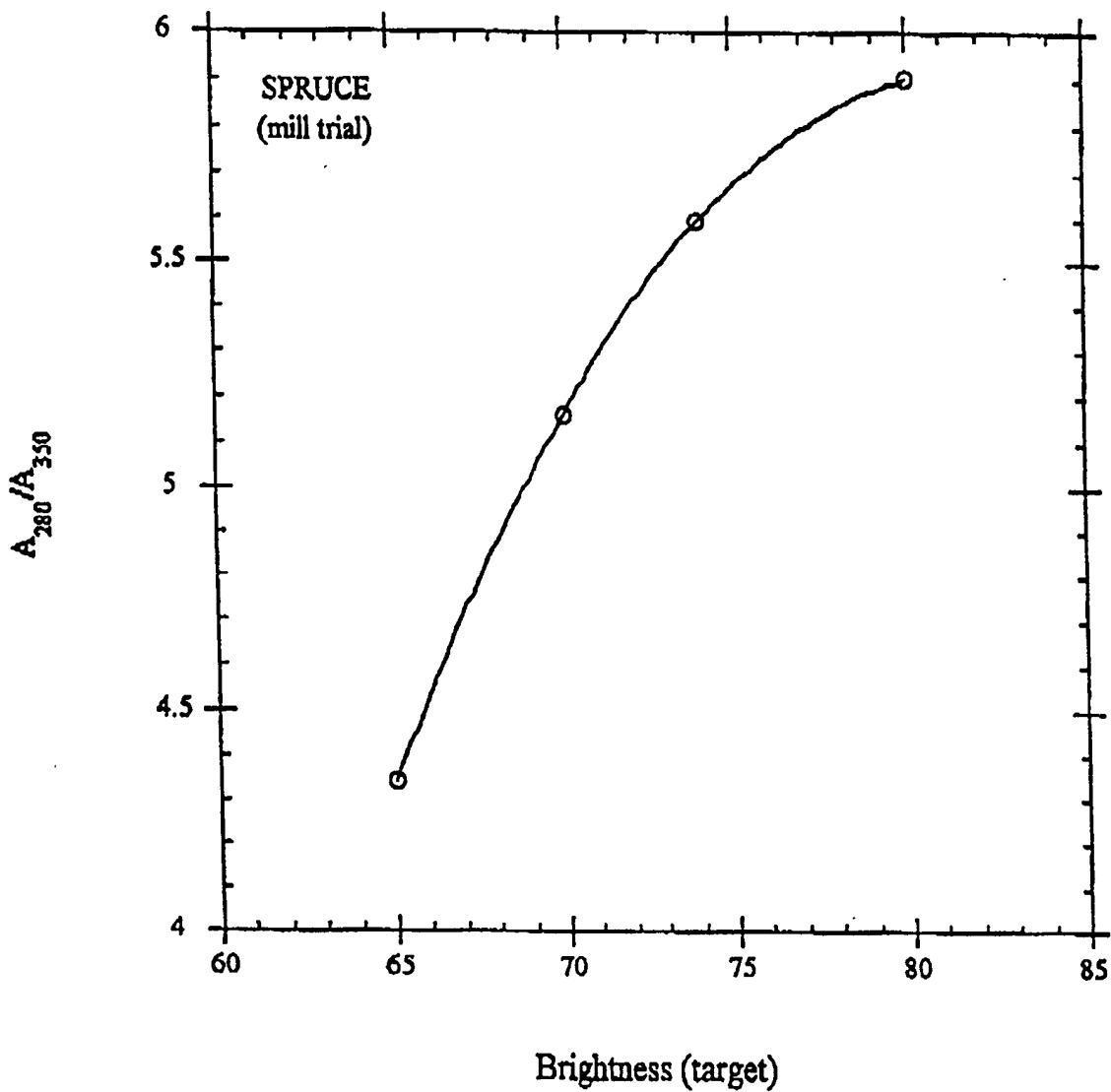


Figure 4. Absorbance ratio A_{280}/A_{350} at 2 minutes after the start of the H_2O_2 brightening reactions as a function of the final target brightness for spruce pulp.

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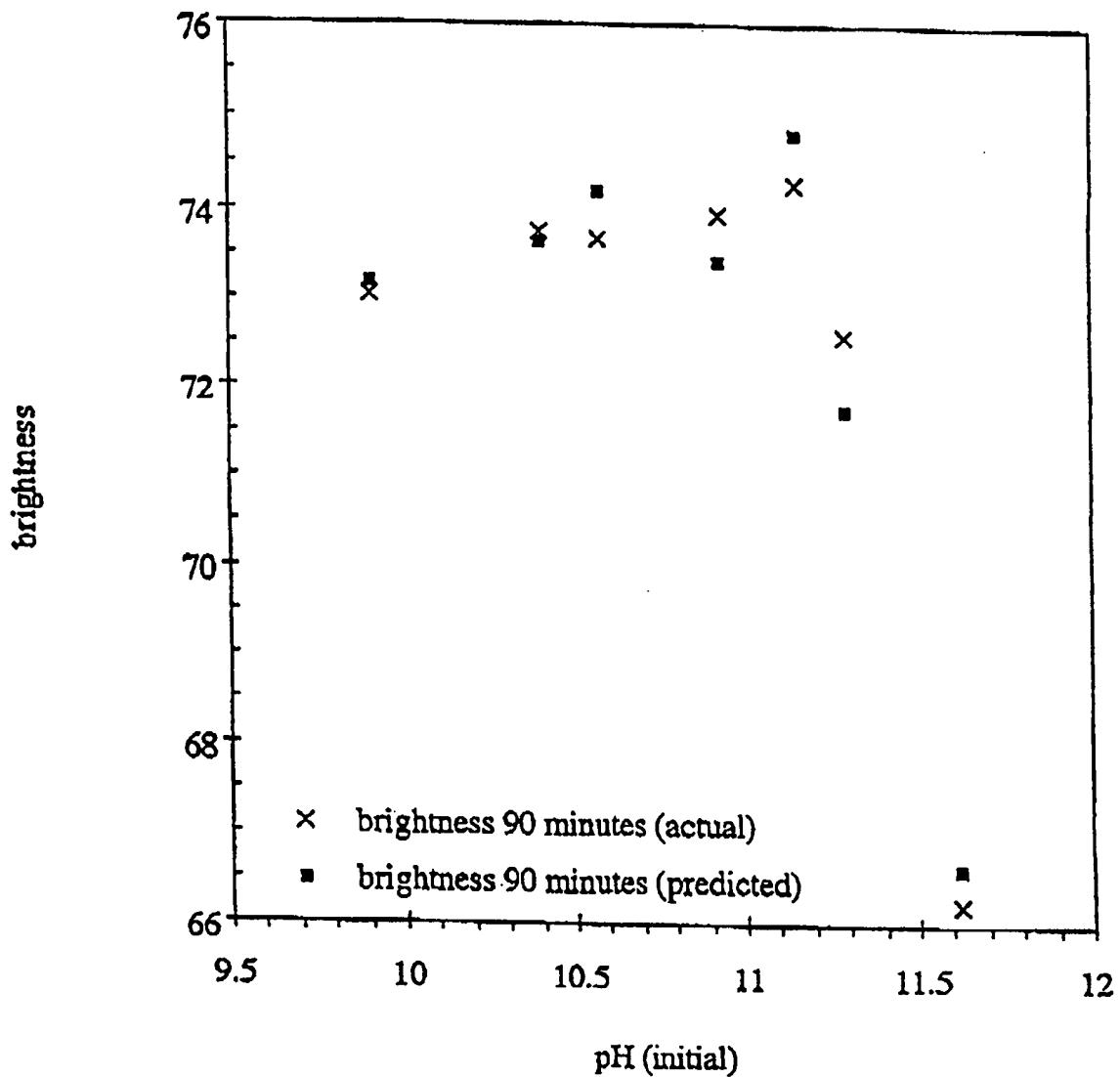


Figure 5. Brightness of spruce pulp at 90 minutes predicted using a multilinear regression with UV ratios taken from the effluent at 3 minutes. The relationship is:

$$\text{brightness} = 95.75 + 44.99 \cdot A_{130}/A_{250} - 322.6 \cdot A_{360}/A_{280} - 4.980 \cdot A_{250}/A_{300}$$

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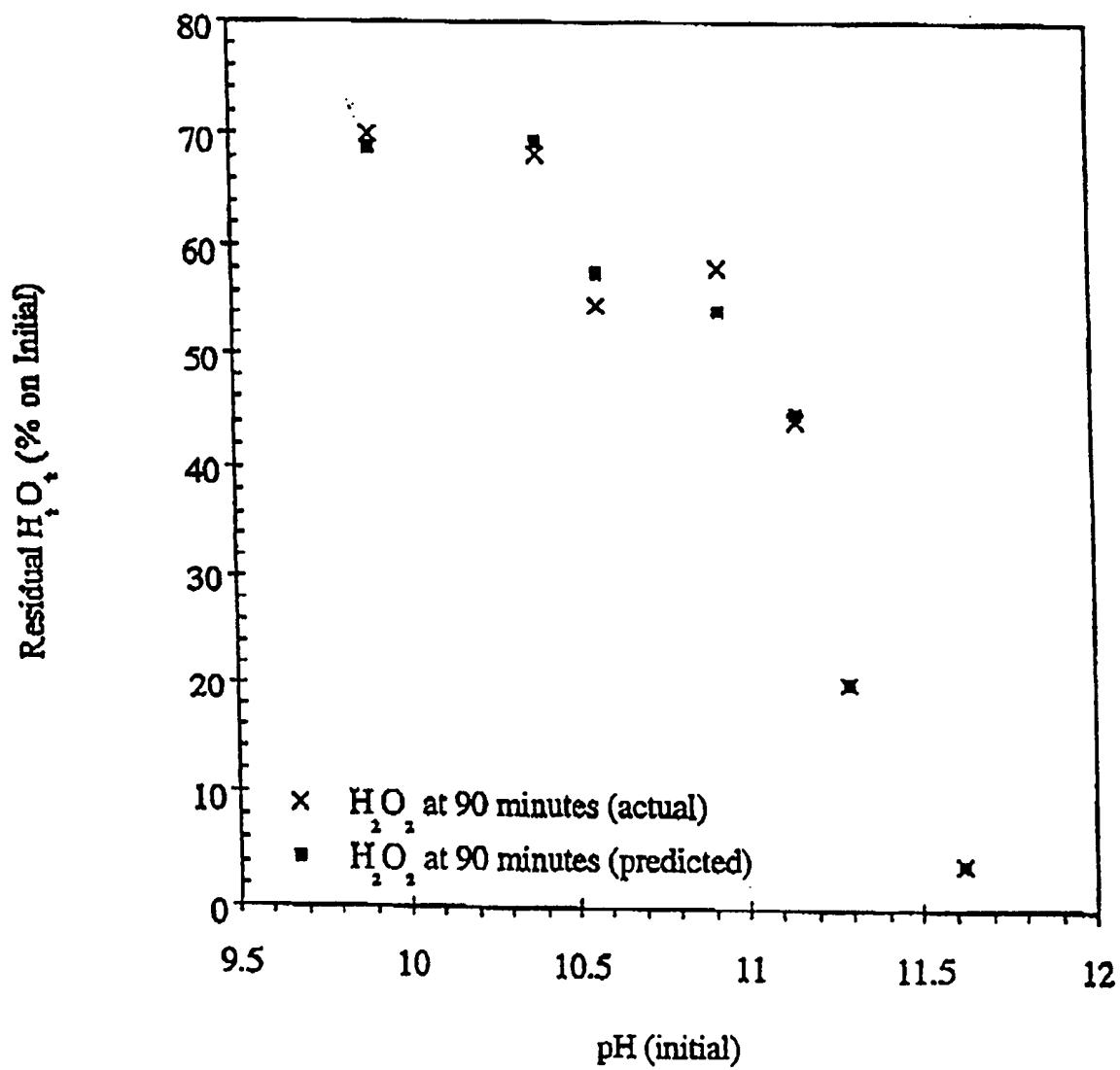


Figure 6. Residual peroxide at 90 minutes predicted using a multilinear regression with UV ratios taken from the spruce pulp H₂O₂ effluent at 3 minutes. The relationship is:
$$\text{residual H}_2\text{O}_2 = 511.00 + 104.24 \cdot A_{230}/A_{250} - 5130.7 \cdot A_{350}/A_{280} + 1521.3 \cdot A_{350}/A_{300}$$

x5

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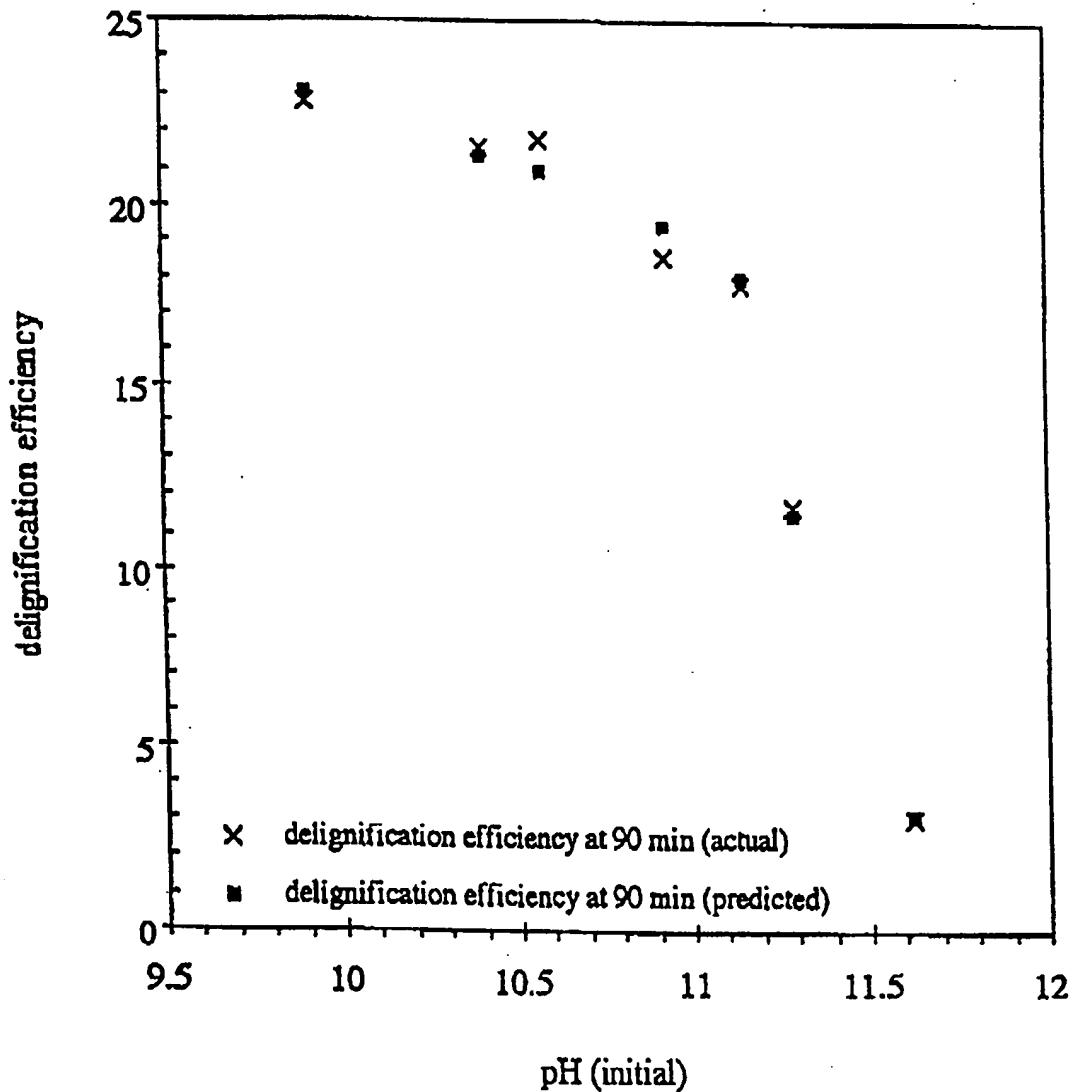


Figure 7. Delignification efficiency for 0- 90 minutes predicted using a multilinear regression with UV ratios taken from the spruce pulp H₂O₂ effluent at 3 minutes. The relationship is:
delignification efficiency = 151.01 + 62.253*A₂₃₀/A₂₈₀ - 772.08*A₃₃₀/A₂₈₀ - 94.107*A₃₀₀/A₂₈₀.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 98/00243

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N21/33 D21C9/10

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 12183 A (EKA NOBEL AB) 25 April 1996 see page 13 - page 14 ---	1-14, 36-49
X	DATABASE WPI Section Ch, Week 8220 Derwent Publications Ltd., London, GB; Class F09, AN 82-40955E XP002073358 & SU 848 515 B (LENINGRAD CELL-PAPER INS) see abstract ---	1,3,7,8, 19,20, 36,38, 42,43, 54,55
A	DE 39 01 662 A (KAJAANI ELECTRONICS) 27 July 1989 see the whole document ---	1-70 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

³ Special categories of cited documents :

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- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

31 July 1998

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INTERNATIONAL SEARCH REPORT

Int	tional Application No
PCT/CA 98/00243	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 01560 A (TECATOR AB) 12 January 1995 see the whole document -----	1-70

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/CA 98/00243

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